ELECTROSYNTHESIS OF ELECTROACTIVE METAL–METAL BONDED POLYMERS [Ru(CO)$_2$L]$_n$ (L = 2,2′-BIPYRIDINE DERIVATIVES), THEIR CHARACTERIZATION AND CATALYTIC ACTIVITY. A REVIEW

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Dedicated to the memory of the late Professor Antonín A. Vlček.

This paper presents an account on the preparation, characterization and properties of conductive polymers [Ru(CO)$_2$L]$_n$ (L = 2,2′-bipyridine derivatives). These strongly adherent and highly colored films containing Ru chains are unique examples of a new generation of organometallic polymers that possess interesting catalytic properties. The formation of these materials from mononuclear complexes like [RuCl$_2$(CO)$_2$L] and their properties were investigated by combined electrochemical techniques and UV-VIS, NMR, FTIR and EPR spectroscopies. The polymer is produced by electrochemically induced propagation involving the intermediate formation of dimers, tetramers and higher oligomers. The air sensitivity of this kind of Ru(0) polymers can be overcome by using polypyrrole matrix with L-attached mononuclear [RuCl$_2$(CO)$_2$L] precursor complexes. A following cathodic step leads, within the polypyrrole film, to the intended second polymer with Ru–Ru bonds. The morphology of this unusual hybrid polymer, investigated by scanning electron microscopy, revealed a uniform material. Regular films are formed by electrodeposition on carbon fibers. Most of these polymers possess high and selective catalytic activity in the electroreduction of carbon dioxide in aqueous media. A review with 36 references.

1. INTRODUCTION

Polymers containing metal–metal bonds in the polymer backbone are expected to possess peculiar conductive and photochemical properties. In this area, however, considerable synthetic efforts are demanded since only little work has been carried out so far[1]. In this context we have developed[2,3] a novel kind of organometallic polymer based on chains of ruthenium atoms. The low metal oxidation state and two vacant coordination sites, required for the metal chain formation, can be easily achieved by electrochemical reduction of a mononuclear precursor complex. The reduction is associated with decoordination of two labile ligands. The overall polymerization process is somewhat reminescent of the well-established formation of organic polymers by electroreduction of dihalo compounds[4–7].

The original principle has been successfully applied to the preparation of some $[Ru^0(CO)_2L]_n$ polymers (L = bidentate nitrogen ligand). The latter materials can be easily prepared as thin films on conductive supports by electroreduction of *e.g.* $[Ru^{II}Cl_2(CO)_2L]$. The polymers proved to be highly selective and efficient catalysts for electroreduction of carbon dioxide in aqueous media[2,3,8] and also for the water gas shift reaction[9] (WGSR). Furthermore, they also exhibit interesting photochemical properties[10].

In order to summarize the results of our investigations, spread in the literature in numerous papers published during the last decade, we trust it is useful to present here an account on the electrochemical synthesis and redox properties of this unique kind of metal–metal bonded polymers, together with their principal physical and chemical characterizations. Their catalytic activities in the reduction of carbon dioxide and oxidation of carbon monoxide will also be reviewed.

2. ELECTROSYNTHESIS OF ORGANOMETALLIC POLYMER FILMS $[Ru(CO)_2L]_n$

The electrosynthesis of ruthenium(0) organometallic polymers containing Ru–Ru bonds, with general formula $[Ru(CO)_2L]_n$ (L = 2,2′-bipyridine (bpy) Chart 1) was carried out some years ago[11,12].

The polymer can easily be obtained as a thin film deposited on electrode surface by a two-electron reductive polymerization process of a precursor mononuclear ruthenium(II) complex such as $[RuCl_2(CO)_2L]$, where L is bpy (L^1), its derivatives (L^2–L^8) and also phenanthroline (L^9, L^{10}) ligands (Chart 1).

L^1, R^1 = H

L^2, R^1 = CH_3

L^3, R^1 = *t*-Bu

L^4, R^1 = $COOCH_3$

L^5, R^1 = COOiPr

L^6, R^1 = $CONH$-C_6H_3-2,4-$(OCH_3)_2$

L^7, R^1 = NO_2

L^8

L^9, R^2 = H
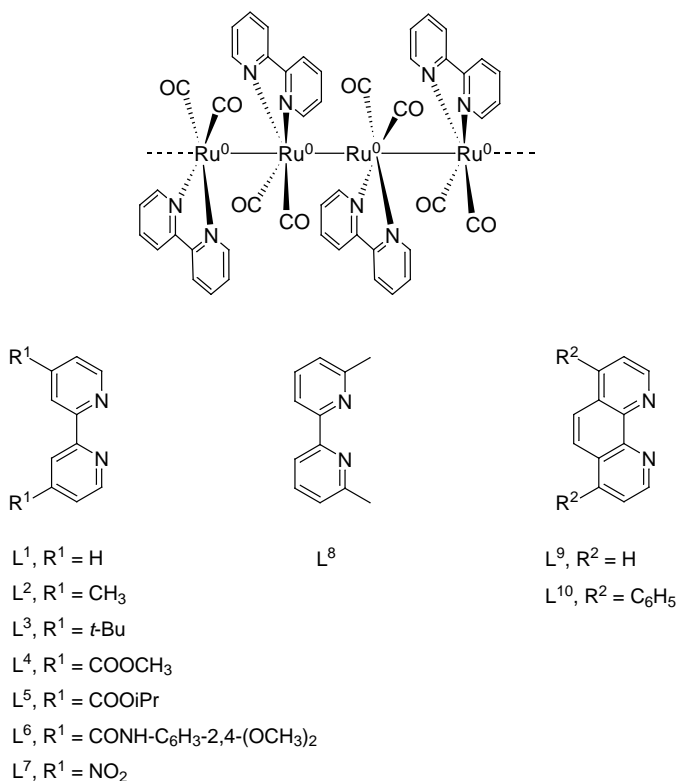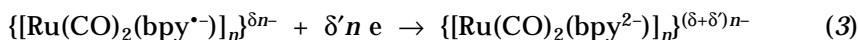
L^{10}, R^2 = C_6H_5

CHART 1

The electrochemical process, leading to a dark-blue electroactive polymeric film strongly adherent to the working electrode surface, is accompanied by the release of two Cl^- anions per molecule of the precursor. The overall electropolymerization process is summarized by Eq. (*1*).

$$n\ [Ru^{II}Cl_2(CO)_2L]\ +\ 2n\ e\ \rightarrow\ [Ru^0(CO)_2L]_n\ +\ 2n\ Cl^- \tag{1}$$

Figure 1 shows the cyclic voltammogram (CV) of *trans*-(Cl)-[RuCl₂(CO)₂(bpy)] (**1**). It exhibits a nearly two-electron irreversible cathodic peak at –1.52 V (denoted p_1) associated with an irreversible anodic peak at –0.72 V (p_1') on the reverse scan[13]. The shape of this cathodic–anodic peak system is typical of an electroprecipitation–redissolution phenomenon. Iterative cyclic voltammetry or controlled-potential electrolysis at –1.65 V induce the electro-

polymerization. This process is evidenced by the regular growth of the electro-activity of the $[Ru(CO)_2(bpy)]_n$ film which is continuously deposited on the working electrode surface (Fig. 2a).

Figure 2b illustrates the redox properties of the resulting polymer after its transfer into an electrolyte solution. The electroactivity persists when scan limit potentials are properly chosen, and is essentially characterized by three redox systems. Two of them at $E_{1/2} = -1.51$ V (p_2, p'_2) and $E_{p,c} = -1.90$ V (p_3) are cathodic and correspond to the consecutive one-electron reductions of the bpy ligands in the film, as described by Eqs (2) and (3).

$$[Ru(CO)_2(bpy)]_n + \delta n\, e \rightarrow \{[Ru(CO)_2(bpy^{\bullet-})]_n\}^{\delta n-} \qquad (2)$$

$$\{[Ru(CO)_2(bpy^{\bullet-})]_n\}^{\delta n-} + \delta' n\, e \rightarrow \{[Ru(CO)_2(bpy^{2-})]_n\}^{(\delta+\delta')n-} \qquad (3)$$

The anodic system at $E_{1/2} = -0.92$ V (p_4, p'_4) is attributed to the partial oxidation of the ruthenium(0) centres in the polymer ($Ru^{0/I}$) (Eq. (4)).
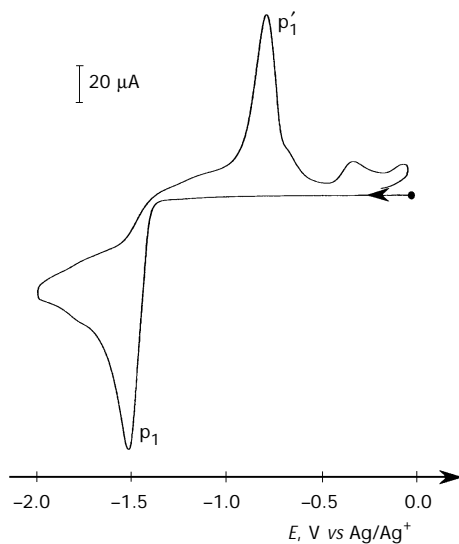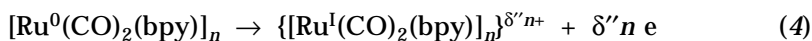

FIG. 1
Cyclic voltammogram of $1 \cdot 10^{-3}$ M **1** in $CH_3CN/1 \cdot 10^{-1}$ M Bu_4NClO_4; $v = 100$ mV s^{-1}, Pt disc electrode ($r = 2.5$ mm)

$$[Ru^0(CO)_2(bpy)]_n \rightarrow \{[Ru^I(CO)_2(bpy)]_n\}^{\delta''n+} + \delta''n\,e \qquad (4)$$

The doping levels δ'' and δ for the metal- and bpy-based, respectively, redox systems were estimated in the film; they are lower than 0.1 per repeating unit[11].
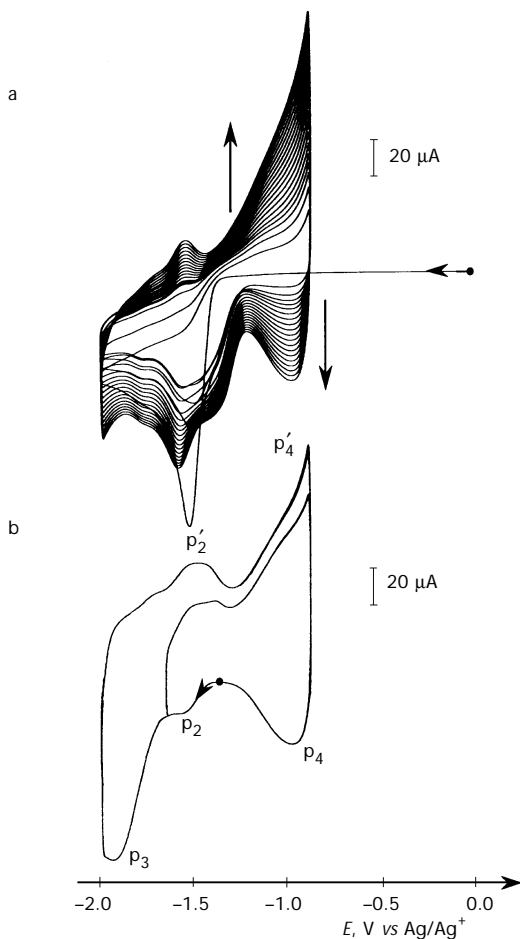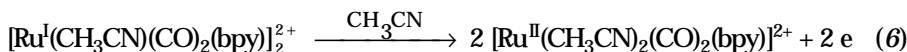

FIG. 2
a Consecutive cyclic voltammograms of **1**, experimental conditions as in Fig. 1. b Cyclic voltammograms at the resulting Pt|[Ru(CO)$_2$(bpy)]$_n$-modified electrode

The organometallic polymer is irreversibly oxidized at potentials higher than −0.85 V. For instance, consecutive scans beyond the oxidation-desorption potential result in fast and progressive disappearance of the initial strong oxidation peak at −0.72 V (p_1') and desorption of the polymer film (Fig. 3, part *b*). The complete two-electron oxidation of the polymer, inducing cleavage of all Ru–Ru bonds, proceeds *via* two consecutive one-electron oxidations of the central Ru atoms according to the Eqs (*5*) and (*6*).

$$[Ru^0(CO)_2(bpy)]_n \xrightarrow{\ CH_3CN\ } n/2\ [Ru^I(CH_3CN)(CO)_2(bpy)]_2^{2+} + n\ e \qquad (5)$$

$$[Ru^I(CH_3CN)(CO)_2(bpy)]_2^{2+} \xrightarrow{\ CH_3CN\ } 2\ [Ru^{II}(CH_3CN)_2(CO)_2(bpy)]^{2+} + 2\ e \quad (6)$$

In practice, the first exhaustive one-electron oxidation of the $[Ru(CO)_2(bpy)]_n$ film at 0.6 V in acetonitrile electrolyte, leads to the formation of the soluble dimeric complex *trans*-(CH_3CN)-$[Ru(CH_3CN)(CO)_2(bpy)]_2^{2+}$. The properties of the latter bis(acetonitrile) dinuclear Ru(I) complex match very well with those of a chemically generated sample that has also been characterized by X-ray diffraction[14].
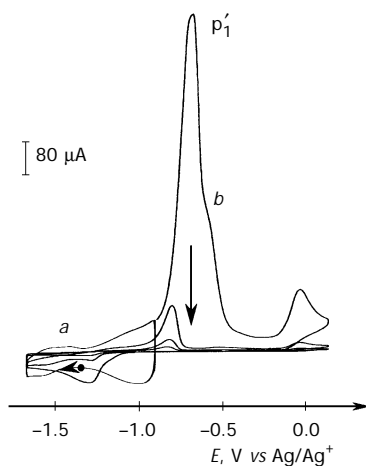

FIG. 3
Cyclic voltammograms of $[Ru(CO)_2(bpy)]_n$ deposited at a Pt disc electrode; experimental conditions as in Fig. 1

The one-electron oxidation of the dimer at 1.0 V induces cleavage of the Ru–Ru bond and produces the mononuclear ruthenium(II) complex $[Ru(CH_3CN)_2(CO)_2(bpy)]^{2+}$ that possesses unexpected *cis*-(CH_3CN) configuration. Its characterization and comparison with the *trans*-isomer described elsewhere support unambiguously this assigment[15,16].

Other derivatives of $[Ru(CO)_2L]_n$ are easily obtained when electron-donating (L^2, L^3) or withdrawing (L^4–L^6) substituents are present in the bpy ligand in positions 4 and 4′, with the exception of the nitro substituted ligand L^7. The latter ligand stabilizes the reduced forms of the parent dichloro Ru(II) complex due to efficient delocalization of the added electron on the bidentate ligand, thereby preventing the formation of the polymer. It has also been shown that the substitution of the bipyridine ligand in positions 6 and 6′ with a relatively bulky group (L^8) does not inhibit the polymerization process. Table I collects the electrochemical data for the ruthenium complexes studied. Precursors containing other leaving groups than Cl⁻ ligands give the same $[Ru(CO)_2(bpy)]_n$ films, as was demonstrated for CH_3CN, $CH_3CO_2^-$, $CF_3SO_3^-$ or SCN^- ligands[11].

Furthermore, the two-electron reduction of the bis(bipyridine) complex *cis*-$[Ru(CO)_2(bpy)_2]^{2+}$ also produces the $[Ru(CO)_2(bpy)]_n$ polymer[17]. In this case the polymerization process is associated with the loss of one bpy ligand (Eq. (7)).

$$n\ [Ru^{II}(CO)_2(bpy)_2]^{2+}\ +\ 2n\ e\ \rightarrow\ [Ru^0(CO)_2(bpy)]_n\ +\ n\ bpy \qquad (7)$$

The crucial point for the formation of the polymeric structure is the presence of two leaving groups. For instance, the mononuclear complex $[RuCl(CO)_2(bpy)\{C(O)OCH_3\}]$ bearing the methoxycarbonyl group, a poor leaving group compared to the Cl⁻ ligand, only undergoes an irreversible one-electron electrochemical dimerization reaction[12]. The corresponding dimer has been isolated and characterized. It does not further polymerize and exhibits a quasi-reversible one-electron reduction at a more negative potential.

At this stage, it should be recalled that the mononuclear precursor $[RuCl_2(CO)_2(bpy)]$ exists in two stereoisomeric forms having *trans*-Cl/*cis*-CO (**1**) and *cis*-Cl/*cis*-CO (**2**) configurations. These two stereoisomers can be easily distinguished by their ¹H NMR parameters[12]. In its negative region, the CV of **2** resembles that of **1**, with an electroprecipitation–redissolution phenomenon. Iterative cyclic voltammetry or controlled-potential electrolysis

TABLE I
Electrochemical data for *trans*-(Cl)-[RuCl$_2$(CO)$_2$L] complexes and corresponding [Ru(CO)$_2$L]$_n$ polymers[a]

Ligands	[RuCl$_2$(CO)$_2$L]	[Ru(CO)$_2$L]$_n$			
	Ru$^{II/0}$	Ru$^{I/0}$	Ru$^{II/0}$	L$^{0/\bullet-}$	L$^{\bullet-/2-}$
	$E_{p,c}$, V[b]	$E_{p,c}$, V[b]	$E_{p,a}$, V[b,c]	$E_{1/2}$, V[b]	$E_{1/2}$, V[b]
L^1	−1.52	−0.92	−0.70	−1.51	−1.90
L^2	−1.58	−1.09	−0.85	−1.33	[d]
L^3	−1.65	–	−1.24	−1.35	−2.18[e]
L^4	−1.26	–	−0.48	−1.25	−1.66
L^5	−1.28	–	−0.38	−1.28	−1.59
L^6	−1.34	−0.72	−0.59	−1.36	−1.65
L^7	−0.77[f]	–	–	–	–
	−0.93[f]				
	−1.12[f]				
	−1.25[f]				
L^8	−1.51	−1.10	−0.74	−1.34	−2.05
L^9	−1.54	−0.91	−0.93	−1.52	[d]
L^{10}	−1.54	−1.04	−0.67	−1.93	[d]

[a] The potentials are referenced to Ag|1 · 10^{-2} M AgNO$_3$ in CH$_3$CN/1 · 10^{-1} M Bu$_4$NClO$_4$ and determined by cyclic voltammetry at 100 mV s^{-1} in CH$_3$CN/1 · 10^{-1} M Bu$_4$NClO$_4$ on a Pt disc electrode[13]. [b] $E_{1/2} = (E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials. [c] Potential of the largest anodic peak observed during the anodic scan limited at 0 V. [d] Poorly resolved peak system. [e] Irreversible redox process ($E_{p,c}$). [f] $E_{1/2}$ value for a reversible redox process.

induce the formation of the same polymer $[Ru(CO)_2(bpy)]_n$ (ref.[12]). It should be noted that a slight shift (–40 mV) of the reduction peak potential of **2** is observed compared with the value obtained for **1**. This implies that the electron density inherent to the reduction process is localized on the bidentate bipyridyl ligand since it is hardly influenced by the structure of the complex (see Section 4).

3. PHYSICAL AND CHEMICAL CHARACTERIZATION OF $[Ru(CO)_2L]_n$ FILMS

The reduced form of the polymeric films can be characterized by EPR spectroscopy. For instance, Fig. 4 shows EPR spectrum recorded after microelectrolysis of $[Ru(CO)_2(L^{10})]_n$ film at $E = -1.9$ V, corresponding to the redox system localized on the ligand L^{10} (Eq. (2)). At this potential, the coordinated radical anions $[L^{10}]^{\bullet-}$ are electrogenerated. The sharp and symetrical EPR signal at $g = 2.0034$ (Fig. 4) indeed points to a paramagnetic species with the unpaired electron localized predominantly on the lowest π^* orbital of L^{10}. The absence of hyperfine splitting is due to some intramolecular electron hopping between two closed ligands. This effect has been reported previously for reduced forms of bipyridine ruthenium complexes in solution[18], or for conductive polymers like polypyrrole or polythiophene[19]. Finally, it should be noted that the polymer films in their neutral state are EPR silent.
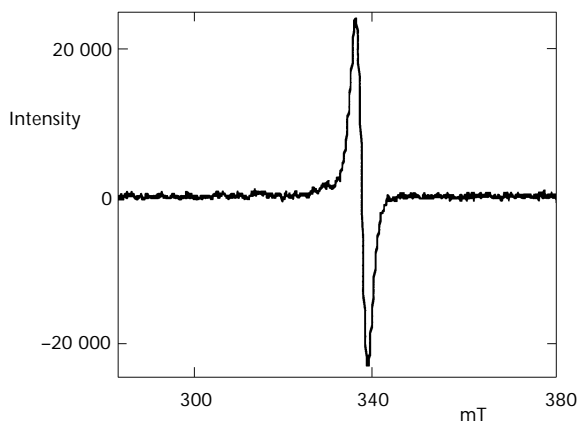

FIG. 4
EPR spectrum of one-electron reduced $[Ru(CO)_2(L^{10})]_n$ on a Pt-wire electrode, recorded at 100 K

Full characterization of $[Ru(CO)_2L]_n$ films is difficult to obtain since they are insoluble in most common solvents and air-sensitive. However, the molecular structure of $[Ru(CO)_2L]_n$ is strongly supported by detailed analysis in the solid state. First, the elemental analysis is consistent with the suggested formulation $[Ru(CO)_2L]_n$. Further, FAB-MS studies on polymer powders show main patterns corresponding to well defined fragments with the expected calculated isotopomer distribution[2,11]. The study of absorption properties of the films can be performed in UV-VIS spectroelectrochemical experiments using modified optically transparent electrodes (OTE). During the electropolymerization process, the intensities of the low-lying absorption bands grow regularly with the thickness of the film. Rising curves in Fig. 5a document this growth in the formation of the polymer deposit[11]. The spectrum of the latter film exhibits one major intense band in the visible region around 790 nm (Fig. 5b), typical for metal-to-ligand charge transfer transition in complexes containing metal–metal bonds[11]. IR spectroscopy also revealed the presence of metal–metal bonds. Low-energy vibrations are observed around 170 cm^{-1} for $[Ru(CO)_2(bpy)]_n$, a value close to that found for $[Ru_3(CO)_{12}]$ (ref.[20]). No bands due to ν(Ru–Cl) vibration are detected in the range of 300–400 cm^{-1}. In addition, the films exhibit several ν(CO) vibrations between 1 920 and 2 010 cm^{-1} and typical bands due to the vibrations of the bpy ligand in the 1 620–1 540 cm^{-1} region. The fact that quantitative desorption and two-electron oxidation of $[Ru(CO)_2L]_n$ produces the soluble *cis*-(CH_3CN)-$[Ru(CH_3CN)_2(CO)_2L]^{2+}$ strongly supports the suggested structure, and emphasizes that only simple chemical reactions, such as metal–metal bond formation without loss of CO or bpy ligands, occur during the electropolymerization process. The morphology of the film $[Ru(CO)_2L]_n$ has been examined by scanning electron microscopy. The surface of the film exhibits a quasi-homogeneous distribution of the polymer with a cotton flower texture. The presence of ruthenium atoms is confirmed by a strong signal observed at 2.5 keV in EDXRA experiments[8].

4. MECHANISM OF ELECTROPOLYMERIZATION

We have demonstrated[21] that polymerization occurs upon reduction of **1** by an electrochemical propagation process (Eqs (*8*)–(*11*)).
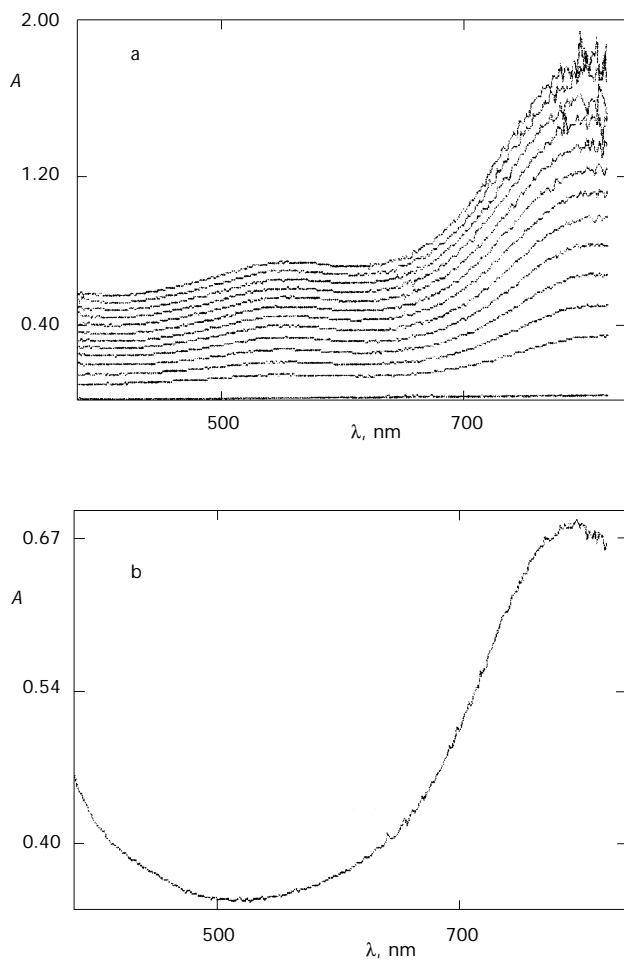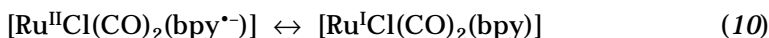
$$[Ru^{II}Cl_2(CO)_2(bpy)] \; + \; e \; \rightarrow \; [Ru^{II}Cl_2 \, (CO)_2(bpy^{\bullet-})]^- \qquad\qquad (8)$$
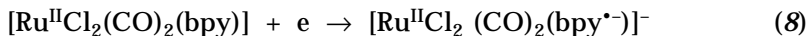
FIG. 5

a Development of the UV-VIS spectra of $[Ru(CO)_2(L^2)]_n$ on an OTE during the electropolymerization of *trans*-(Cl)-$[RuCl_2(CO)_2(L^2)]$ in $CH_3CN/1 \cdot 10^{-1}$ M Bu_4NClO_4. b UV-VIS spectrum of the resulting polymer film

$$[Ru^{II}Cl_2(CO)_2(bpy^{\bullet-})]^- \rightarrow [Ru^{II}Cl(CO)_2(bpy^{\bullet-})] + Cl^- \qquad (9)$$

$$[Ru^{II}Cl(CO)_2(bpy^{\bullet-})] \leftrightarrow [Ru^{I}Cl(CO)_2(bpy)] \qquad (10)$$

$$[Ru^{I}Cl(CO)_2(bpy)] \rightarrow dimer \rightarrow tetramer \rightarrow [Ru(CO)_2(bpy)]_n \qquad (11)$$

This is a consequence of the lower reduction potentials for the dimer and concomitantly formed tetramer and higher oligomers. An electrochemical study conducted on the independently chemically prepared $[RuCl(CO)_2(bpy)]_2$ dimer[22] has demonstrated that the latter complex is reduced at a less negative cathodic potential ($E_{p,c}$ = –1.46 V) than the precursor **1** ($E_{p,c}$ = –1.52 V)[21].

In terms of mechanism it means that the polymerization proceeds *via* the initial formation of the unstable radical anion with the singly reduced bpy ligand (Eq. (*8*)) that loses a Cl⁻ ligand and transforms to a coordinatively unsaturated Ru^I species (Eqs (*9*) and (*10*)). This unstable 17-electron species dimerizes and the resulting dimer is rapidly reduced at the applied reduction potential of the parent mononuclear dichloro complex (Eq. (*11*)).

This mechanism has received further support from redox studies of the corresponding osmium complex *trans*-(Cl)-[OsCl$_2$(CO)$_2$(bpy)] (ref.[23]). The cathodic region of the CV for this mononuclear Os(II) complex in acetonitrile is very similar to that of **1** (Fig. 1), exhibiting irreversible nearly two-electron reduction. Interestingly, electrochemical experiments conducted in a less dissociating and coordinating solvent (such as THF) show that the [OsCl$_2$(CO)$_2$(bpy$^{\bullet-}$)]⁻ radical anion is stable on the subsecond CV time scale at ambient temperature. However, exhaustive electrolysis yields again the [Os(CO)$_2$(bpy)]$_n$ polymer. It should be noted that **1** is irreversibly reduced in both THF and CH$_3$CN solutions, indicating a weaker Ru–Cl bond compared to Os–Cl.

5. IMMOBILIZATION OF ORGANOMETALLIC POLYMER PRECURSORS IN PREFORMED POLYPYRROLE FILMS

The main difficulty concerning the utilization of [Ru(CO)$_2$L]$_n$-modified cathodes arises from their facile oxidation *e.g.* with molecular oxygen, inducing their slow desintegration. In order to avoid the polymer desintegration, a new generation of modified electrodes was created, using

e.g. polypyrrole *N*-functionalized polymers with attached monomeric [$RuCl_2(CO)_2L$] complexes[24]. Polypyrrole (polypyr)-modified electrodes with appended [$RuCl_2(CO)_2L$] units are prepared by an anodic polymerization of the corresponding mononuclear complex containing a polymerizable pyrrole (pyr) function (L^{11} and L^{12}, Chart 2). This anodic polymerization protocol can be obtained either by scanning the potential repeatedly or by controlled-potential electrolysis at the pyrrole oxidation peak. Figure 6a depicts the electropolymerization of [$RuCl_2(CO)_2(L^{12})$]. During potential scans, the reversible peak system of the polypyrrole appears at $E_{1/2} = 0.31$ V
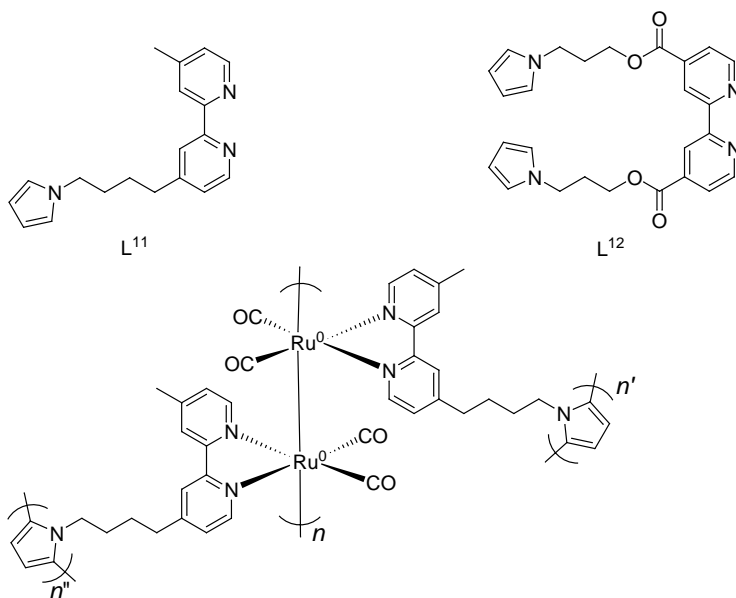

CHART 2

and increases regularly, indicating the growth of polypyr[$RuCl_2(CO)_2(L^{12})$] on the electrode surface. As expected, upon transfer to an electrolyte solution, the polypyrrole film exhibits the normal electroactivity of an *N*-substituted polypyrrole derivative (Fig. 6b, curve *1*). The formation of metal–metal bonds within the polypyrrole film can be easily achieved electrochemically by cycling the potential of the Pt- or GC|polypyr[$RuCl_2(CO)_2L$]-modified electrode (GC stands for glassy carbon) in the cathodic range. The initial intense cathodic peak at –1.2 V of the polypyr[$RuCl_2(CO)_2(L^{12})$] film (Fig. 6b, curve *2*) is replaced with several quasi-reversible systems. The

electroinduced formation of Ru–Ru bonds in the film is confirmed by spectroelectrochemical experiments. While the initial polypyr[RuCl$_2$(CO)$_2$(L^{12})] film does not absorb at wavelengths longer than 500 nm, at –1.4 V the film exhibits a strong broad absorption between 600 and 800 nm. The proposed structure of the polypyr[Ru(CO)$_2$(L^{11})]$_n$ composite material is depicted in Chart 1.
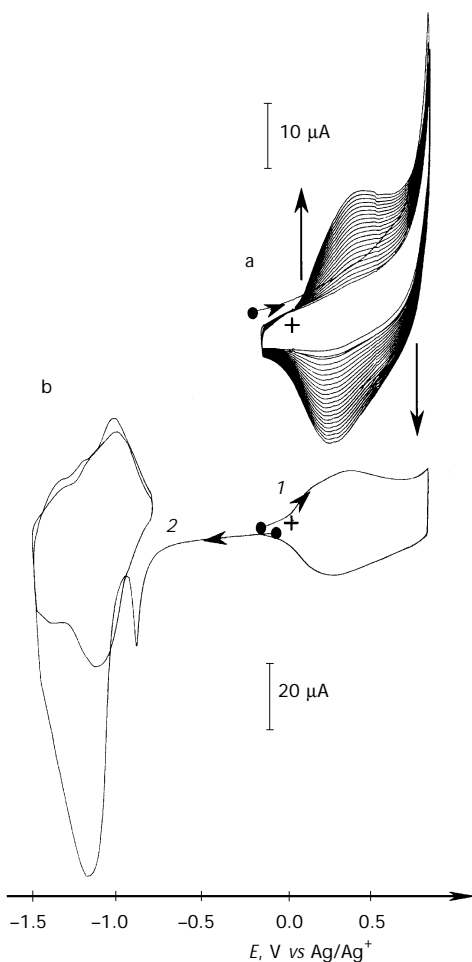

F$_{IG}$. 6
a Cyclic voltammograms recorded during the polymerization of [RuCl$_2$(CO)$_2$(L^{12})] on a glassy carbon electrode by repeated anodic potential scans in CH$_3$CN/1 · 10^{-1} M Bu$_4$NClO$_4$. b Cathodic and anodic potential scans with the resulting polypyrrole-modified electrode in an acetonitrile electrolyte solution

The morphology of polypyrrole films deposited on carbon fibers can be examined by microscopy. A scanning electron micrograph of a polypyr[$RuCl_2(CO)_2(L^{12})$] film deposit is presented in Fig. 7, showing the homogeneity and regularity of the electrochemically prepared polymer when carbon fibers are used as supporting material.

6. ELECTROCATALYTIC ACTIVITY OF [$Ru(CO)_2L$]$_n$ FILMS IN CO_2 REDUCTION

The interest in the electrocatalytic reduction of CO_2, aimed at the construction of artificial photosynthetic systems and environmental applications, has been increasing rapidly in the last decade[25,26]. A large variety of transition metal complexes has been studied as electrocatalysts[27,28]; however, only few appear to be effective in aqueous electrolytes. The simultaneous reduction of protons limits the efficiency of the electrocatalysis. A solution to this problem is to use complexes immobilized on metallic cathode surfaces. Some attempts have been reported recently in the literature, but the success obtained with this type of devices remains scarce.

For example, electrocatalytic CO_2 reduction on a graphite electrode, coated with a cobalt phthalocyanine incorporated in a membrane, produced CO with a high selectivity (CO/H_2 = 6) at –1.2 V *vs* Ag/AgCl (pH 5)[29]. An electropolymerized film of a chromium–vinylterpyridine complex exhibits[30] efficient catalytic performance in electroreduction of CO_2 to formaldehyde (87% current efficiency) at –1.1 V *vs* Ag/AgCl. Utilization of an iron(II) complex, immobilized in a polyaniline/Prussian Blue laminated
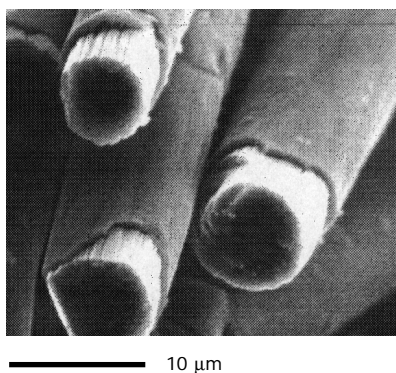

———— 10 µm

FIG. 7
Scanning electron micrograph (× 3 000) of polypyr[$RuCl_2(CO)_2(L^{12})$] deposited on carbon fibres

electrode, allows[31] to reduce CO_2 electrochemically into a series of C_1 to C_3 products with a current efficiency up to 40% at –0.8 V *vs* Ag/AgCl.

In this context, we have reported very efficient and selective electro-catalytic reduction of CO_2 at $[Ru(CO)_2L]_n$ films in an aqueous electrolyte at a moderate potential applied[3]. The efficiency and the selectivity of this catalysis has been investigated as a function of several parameters (electrolyte solution, initial pH and nature of the ligand L). It has been found that the selectivity (CO *vs* $HCOO^-$) can easily be tuned by varying this L ligand[8,32].

Figure 8 shows cyclic voltammograms of a $[Ru(CO)_2(bpy)]_n$ film in aqueous medium under Ar (*a*) and CO_2 (*b*). The electroactivity of the modified electrode remains almost identical to that observed in CH_3CN under Ar. Bubbling CO_2 induces a strong shift and increase of the cathodic current, indicating a strong electrocatalytic phenomenon due to carbon dioxide reduction. Electrolysis in a pure aqueous electrolyte solution at –1.2 V on a carbon felt electrode coated with $[Ru(CO)_2(bpy)]_n$ produces[3] CO with current efficiency >97%. The influence of the initial pH of the electrolyte solution was evaluated for several electrolyte solutions. The optimum CO_2 reduction efficiency (98%) at –1.2 V was achieved at pH 6 (citrate buffer/ $1 \cdot 10^{-1}$ M $LiClO_4$). Under more acidic or basic conditions the CO production decreases[8].
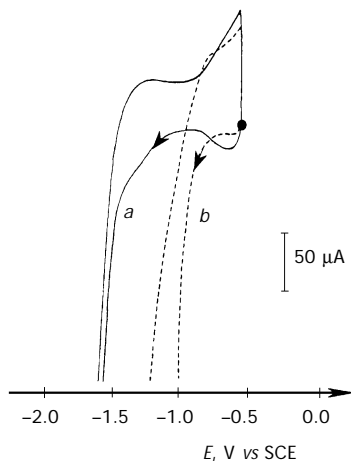

FIG. 8
Cyclic voltammograms of a $[Ru(CO)_2(bpy)]_n$-modified GC electrode in $H_2O/1 \cdot 10^{-1}$ M $LiClO_4$ under Ar (*a*) and CO_2 (*b*)

Taking into account the proposed structure of the polymer film, we suggest the following mechanism for the electrocatalytic process (Scheme 1). The initial step involves a one-electron reduction of the electroactive $[Ru(CO)_2(bpy)]$ unit in the polymeric film to give $[Ru(CO)_2(bpy^{\bullet-})]^-$. As expected, this 19-electron species is not stable and may liberate CO, producing a pentacoordinate species $[Ru(CO)(bpy^{\bullet-})]^-$. In the presence of CO_2 and water, acting as a proton source, the latter unit produces $[Ru(CO)_2(bpy)]^+$ *via* the intermediate formation of $[Ru(CO)(bpy)\{C(O)OH\}]$. At the electrolysis potential, $[Ru(CO)_2(bpy)]^+$ is reduced back to $[Ru(CO)_2(bpy)]$ that is ready to perpetuate the electrocatalytic cycle. Electrogeneration of pentacoordinate metal carbonyl complexes such as $[Ru(CO)(bpy)_2]$ and $[ReCl(CO)_2(bpy)]^-$ has been postulated previously as the key step in homogeneous electrocatalytic processes[33,34].
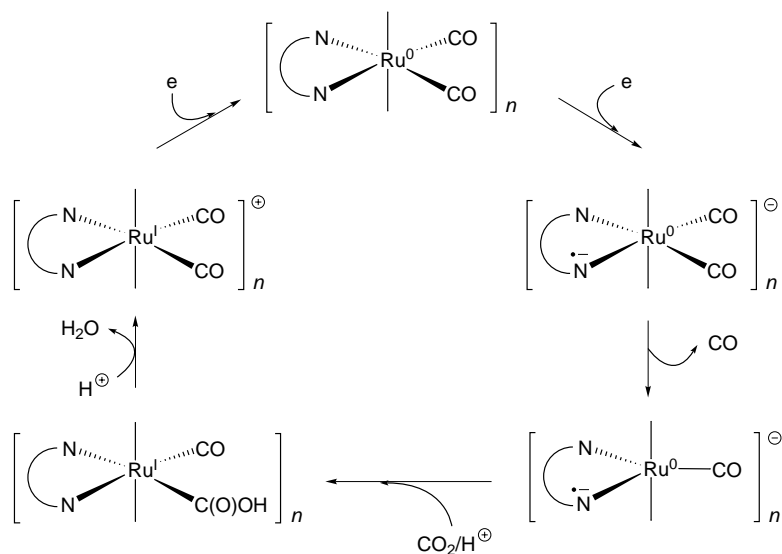
SCHEME 1

As pointed above, an important feature of the $[Ru(CO)_2L]_n$ polymers is that the selectivity of the electrocatalytic reduction of CO_2 can be changed dramatically when films are prepared using a bpy ligand disubstituted in the 4,4′-position with electron-withdrawing groups like in ligands L^4 and L^5. In both these cases, the main product of the CO_2 reduction over a large pH range (pH > 5) is $HCOO^-$ (refs[8,32]). Optimum current efficiency of 90% for $HCOO^-$ formation was obtained at pH 12. Since in this case $HCOO^-$ is

the major reduction product, the operating reaction mechanism is probably different; although, the $[Ru(CO)(L^{\bullet-})]^-$ species should be also considered the key transient. A plausible hypothesis is that CO_2 coordinates at the metal centre in the formate form (M–O–C(O)H) instead of the hydroxycarbonyl form (M–C(O)OH). This formate bond could result from the initial formation of a metal hydride, followed by insertion of CO_2 or by an isomerization of carboxylato metal species to formato complex. A similar mechanism and substituent effect have been postulated for other metal complexes capable of reducing CO_2 into $HCOO^-$ ions rather selectively[35]. Conversely, electron-donating groups such as Me in the bipyridine ligand (L^2) increase the production of CO up to 99%.

The same study has been carried out with $C|polypyr[Ru(CO)_2L]_n$ films with $L = L^{11}$ and L^{12}. As expected, the selectivity of the CO_2 reduction to $HCOO^-$ brought about by the ester groups is maintained in the preformed polypyrrole films. The utilization of these kinds of modified electrodes allows extraordinary stable catalytic currents to be obtained. These electrodes can be reused several times without any change in the intensity of the steady catalytic current. Under these conditions, current efficiency of 99% for formate production can be reached at a very low applied potential (–0.75 V *vs* Ag/AgCl)[32].

7. CATALYTIC ACTIVITY OF $[Ru(CO)_2(bpy)]_n$ IN THE WATER GAS SHIFT REACTION (WGSR)

Chemically-activated silica-supported $[RuCl_2(CO)_2(bpy)]$ is an excellent WGSR catalyst in heterogeneous phase[36]. In this catalytic process, a polymer structure has been proposed for the active species. To clarify that point, WGS experiments were carried out with an electrochemically prepared polymer, $[Ru(CO)_2(bpy)]_n$. Even though this material seems to be a modest catalyst for the WGSR, significant results were obtained[9]. A major drawback of this electrochemically prepared polymer consists in the fact that, owing to its poor solubility in common solvents, it appears difficult to disperse the polymer properly on the activated silica support. This leads to a low-active surface area and limits the catalytic activity. However, this set of experiments has clearly demonstrated the catalytic function of the $[Ru(CO)_2(bpy)]_n$ polymer in the WGSR, formed from $[RuCl_2(CO)_2(bpy)]$ deposited onto silica support pre-treated with diluted NaOH solution[36].

8. CONCLUSION AND OUTLOOK

This account deals with clean preparation of a novel type of organometallic polymer with metal–metal bonds by an electrochemical procedure. This procedure consists of the reduction of metal complex precursors like a ruthenium(II) carbonyl complex containing a bidentate nitrogen ligand. The polymerization occurs through an electrochemical propagation process. This type of molecular polymer materials presents the first example of organometallic polymers containing ordered metal–metal bond chains.

Construction of similar novel polymer films, with different metal centres and/or functionalized with an appropriate ligand, may find multiple potential applications, for example in electrocatalytic devices. Moreover, the design and preparation of novel soluble electroactive polymers will permit better characterization of these original molecular materials.

As an example, the great interest in the $[Ru(CO)_2(bpy)]_n$ polymer films has already resulted in useful electrocatalytic applications. Electrodes modified with these films act as very efficient and selective molecular cathodes for electroreduction of CO_2, in particular in aqueous electrolytes. They display a high selectivity for the process (CO or $HCOO^-$ are formed in quantitative coulomb yield) at an accessible electrode potential; the selectivity can easily be tuned by varying the nature of the bidentate ligands. Moreover, the operational stability of these molecular catalytic materials, under the smooth conditions required for the CO_2 activation, becomes superior when the metal–metal bonds are electrogenerated in preformed polypyrrole films substituted by the precursor complexes.

Further investigations to develop novel catalysts based on the organometallic polymers containing ordered metal–metal bond chains, for the electroreduction of CO_2 into more than two-electron-reduced species, are in progress.

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